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(54) Flash fusible toner

Durch Blitzlicht schmelzbarer Toner

Toneur fusible au flash

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128 558 (HITACHI KASEI KOGYO K.K.)
24-07-1984

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Description

The present invention is concerned with resins for use in toners, particularly flash fusible toners. The toners have the advantage of not producing harmful fumes or odors when flash fused.

US-A-4,416,965 and US-A-32,136 show toners having some structural similarity to those of the present invention. However, none has the unique combination of monomers which result in the superior properties attainable with the flash fusible toner resins described herein. US-A- 3998747 and EP-A- 164257 describe polyester toner binder resins.

The present invention provides a toner binder resin that is particularly suited to application in high speed flash fusing. It has high thermal stability, a low critical surface energy, and can be made in a variety of molecular weights, chain stiffnesses, and gel contents. A toner binder resin to be used in flash fusing should preferably have the following characteristics:

1. Be capable of being synthesized via step-growth polymerization methods, so as to prevent depolymerization to dangerous monomers.
2. Have a glass transition temperature between 60-70°C.
3. Be totally amorphous and friable, to meet jet-milling requirements.
4. Be predominantly of low molecular weight polymer.
5. Be processable via melt processing in the presence of acidic charge control agents.
6. Be compatible with conductive dual component toner/carrier systems.
7. Have the appropriate rheological characteristics to allow for rapid fusing.
8. Be chargeable via tribocharging to form a stable charge that is stable in the presence of high humidity.
9. Be fusible via flash fusing to form a durable, well fused image.
10. Have low critical surface energy to facilitate and promote rapid spreading during fusing of toner on paper.

The present invention meets these requirements. Bisphenol A polyester (BAP) resins containing an aliphatic diacid and sometimes also a hydroxyarene-carboxylic acid are used in flash fusible toner as the binder

resin.

Fig. 1 is a schematic outline of the synthesis and structure of the compounds of the present invention. Bisphenol A is acetylated and the product reacted with an aliphatic diacid to yield copolymers, or with an aliphatic diacid and a hydroxyarene-carboxylic acid (which can be derived from p-acetoxybenzoic acid as shown in Fig. 1) to yield a terpolymer. A partially crosslinked product is prepared when phloroglucinol is included as a monomer.

Polyesters using aliphatic dicarboxylic acids and bisphenol-A often have a low glass transition temperature. Low Tg in toner resin leads to toner filming on carrier and development hardware, and also causes blocking during storage or transport. This problem is solved by using hydroxybenzoic acid as a third monomer. Optimal glass transition temperature and melt viscosity are thus obtained without increasing molecular weight. This toner binder resin fulfills all of the above requirements. This class of material can be prepared readily using widely available inexpensive monomers. The preparation and structure of the resulting polymer is shown in Fig. 1. The superiority over the prior art in polyester toner resins is: (1) lower surface energy afforded by the use of an aliphatic dicarboxylic acid and the diol bisphenol, (2) the absence of toxic compounds generated during flash fusing, and (3) the ability to attain a controlled gel content level.

The critical surface energy as measured by contact angle for BAP is less than 40 dynes/cm which is lower than known styrene/acrylate resins. BAP resin has a 5% weight loss at 340°C which compares to 260°C for PICCO 1200 resin from Hercules. Furthermore, addition polymers will thermally depolymerize to regenerate the monomers. For example, the major degradation products using PICCO 1200 are styrene and n-butylmethacrylate, both of which are toxic, offensive smelling, and have a low flash point. The BAP materials decompose to form a char and very low level of volatile organics.

The polyester from bisphenol A and adipic acid with various third monomers have been prepared by solution and melt polymerization techniques in a number of different molecular weights. The glass transition temperature scales with the intrinsic viscosity which is related to molecular weight. A 10°C increase in Tg is realized with the addition of 13% by mole of p-hydroxybenzoic acid as a third monomer. The polymers retain their glassy amorphous nature with the glass transition temperature of about 64°C. They can be milled, melt processed in the presence of acidic charge control agents, and tribocharged negatively on spherical and irregular carriers. This polymer is insensitive to moisture, and forms a durable fused image. Various polyester resins can be prepared by using different ratios of monomers to achieve different glass transition temperatures as required by the particular electrophotographic printer.

One novel technical advance over previous methods involves the use of bisphenol A monomer to favor

the formation of a glassy amorphous polymer and the use of a nonstoichiometric monomer ratio to control both the molecular weight and end group chemistry, and the use of the third monomer to boost the T_g without raising the molecular weight which would in turn lower the friability and increase the melt viscosity. Also, end-group selectivity is possible in this system permitting the introduction of functionality to effect tribocharging. The use of aliphatic diacids lowers surface energy and the glass transition temperature. Since most polyesters are engineered to produce tough fracture resistant material, there has been little call to produce materials with low fracture energy and amorphous structure. These polymers, to our knowledge, represent a new approach to simultaneously engineering one polymer to meet the many requirements of a flash fusible toner.

Flash fusing presents certain peculiar challenges for a toner binder. This challenge is further increased by the cost consideration, milling rate requirements, and compounding requirements of the existing production facilities. The major difficulty in flash fusing is to obtain a temperature suitable for fusing at the paper/toner interface before the top layer of toner is heated above the temperature at which an unacceptable level of decomposition products are generated. The top layer of the toner is exposed to a much higher temperature than the required melt temperature. Thus there is a need for toner resin materials that melt and flow readily and have high thermal stability. Since spreading is a function of the surface energy of the toner and that of the paper, a further requirement is that the resin have a low critical surface energy. Prior art has used blends of polystyrene acrylate copolymers with heat stable epoxy resins to attain a compromise between thermal stability and low surface energy. Prior art involving Bisphenol A copolymers also report the use of styrene/acrylate blends to obtain adequate performance. The low glass transition of the binary bisphenol-A polymers limits the usefulness in toner application. The present invention addresses all the key functional components of a flash fusing toner resin: low surface energy, T_g in the 60-70°C range, thermal stability with decomposition to nontoxic vapors, and tribocharging.

One preferred variation of the present invention leads to the ability to prepare BAP toner resins with controlled gel content. These nonlinear polyesters are prepared by the inclusion of 0.05 to 10 mol percent of the co-monomer 1,3,5-trihydroxybenzene to the preparation of the above mentioned linear polymer. Results on these partially gelled polyester resins indicate that the inclusion of 1,3,5-trihydroxybenzene into the BAP formula does not detract from the processability, low surface energy, and low volatiles release upon flash fusing which is characteristic of this resin family. In fact, the friability of the resins is improved as compared to the linear resins. Results show that toners prepared with resins containing gelled or crosslinked polymer are particularly resistant to filming onto the carrier in dual com-

ponent developer systems, thus have much longer toner/carrier mix lifetime than toners with linear resin. Additionally, toners prepared from resins containing at least 25% gel content still attain optical densities upon flash fusing of 1.4. This high optical density is attainable with toner coverages of as little as 600 µg/cm².

Claims

1. The use, in an electrophotographic process in which a fused image is formed by flash fusing a toner, of a flash fusible toner comprising a bisphenol-A polyester binder resin, which is the polymerisation product of a monomer mixture of bisphenol A and an aliphatic diacid.
2. A use as claimed in claim 1 wherein the aliphatic diacid is adipic acid.
3. A use as claimed in claim 1 or claim 2 wherein the monomer mixture also comprises a hydroxyarene-carboxylic acid.
4. A use as claimed in claim 3 wherein the hydroxyarene-carboxylic acid is p-hydroxybenzoic acid.
5. A use as claimed in any preceding claim wherein from 0.05 to 10 mol percent of 1,3,5-trihydroxybenzene is added to the monomer mixture.
6. A flash fusible toner comprising a binder resin which is the polymerisation product of a monomer mixture of bisphenol A, an aliphatic diacid and a hydroxyarene-carboxylic acid.
7. A toner as claimed in claim 6 wherein 0.05 to 10 mol percent of 1,3,5-trihydroxybenzene is added to the monomer mixture.

Patentansprüche

1. Verwendung eines mit einem Flammblitz aufschmelzbaren Toners in einem elektrophotographischen Verfahren, indem ein aufgeschmolzenes Bild durch das mit einem Flammblitz erfolgende Aufschmelzen eines Toners hergestellt wird, umfassend ein Bindeharz aus Polyester aus Bisphenol-A, das das Polymerisationsprodukt eines Monomergemischs aus Bisphenol A und einer aliphatischen Disäure ist.
2. Verwendung nach Anspruch 1, bei der die aliphatische Disäure Adipinsäure ist.
3. Verwendung nach Anspruch 1 oder 2, bei der das

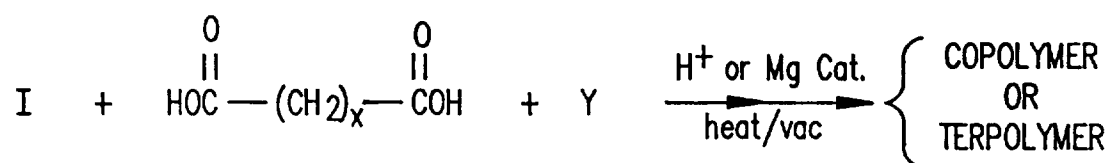
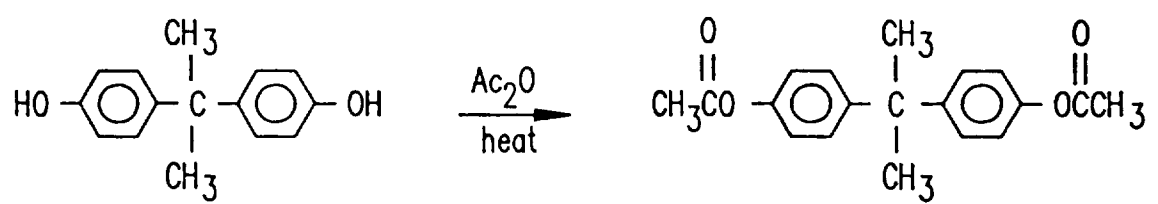
Monomer-Gemisch eine Hydroxyarencarboxylsäure umfasst.

4. Verwendung nach Anspruch 3, bei der die Hydroxyarencarboxylsäure p-Hydroxybenzoesäure ist. 5
5. Verwendung nach einem beliebigen vorhergehenden Anspruch, bei der dem Monomer-Gemisch 0,05 bis 10 Mol-% 1,3,5-Trihydroxybenzol zugesetzt werden. 10
6. Mit einem Flammblitz aufschmelzbarer Toner, umfassend ein Bindeharz, das das Polymerisationsprodukt eines Monomer-Gemischs von Bisphenol A, einer aliphatischen Disäure und einer Hydroxyarencarboxylsäure ist. 15
7. Toner nach Anspruch 6, worin dem Monomer-Gemisch 0,05 bis 10 Mol-% 1,3,5-Trihydroxybenzol zugesetzt werden. 20

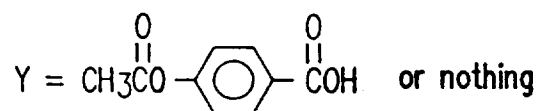
Revendications

1. Utilisation, dans un procédé électrophotographique 25
dans laquelle une image fondue est formée par fusion éclair d'un toner, d'un toner pouvant être fondu par fusion éclair comprenant une résine de liaison de polyester de bisphénol A, qui est le produit de polymérisation d'un mélange de monomères 30
comprenant du bisphénol A et un diacide aliphatique.
2. Utilisation suivant la revendication 1, dans laquelle le diacide aliphatique est l'acide adipique. 35
3. Utilisation suivant les revendications 1 ou 2, dans laquelle le mélange de monomères comprend aussi un acide hydroxyarène carboxylique. 40
4. Utilisation suivant la revendication 3, dans laquelle l'acide hydroxyarène carboxylique est l'acide p-hydroxybenzoïque.
5. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle il est ajouté de 0,05 à 10% en moles de 1,3,5-trihydroxybenzène dans le mélange de monomères. 45
6. Toner pouvant être fondu par fusion éclair comprenant une résine de liaison qui est le produit de polymérisation d'un mélange de monomères comprenant du bisphénol A, un diacide aliphatique et un acide hydroxyarène carboxylique. 50
7. Toner suivant la revendication 6, dans lequel il est ajouté de 0,05 à 10% en moles de 1,3,5-trihydroxybenzène dans le mélange de monomères. 55

SYNTHESIS AND STRUCTURE OF BISPHENOL A POLYESTER
TONER RESINS



$$x = 2, 3, 4$$



Preferred:

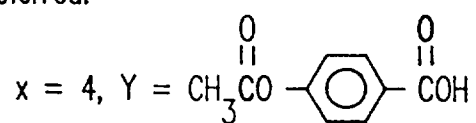


FIG. 1